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US Army Corps of Engineers
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Installation Restoration Research Program

Ion Chromatography with Electrochemical Detection for Hydrazine Quantitation in Environmental Samples

by Steven L. Larson, Ann B. Strong

Prepared for Headquarters, U.S. Army Corps of Engineers

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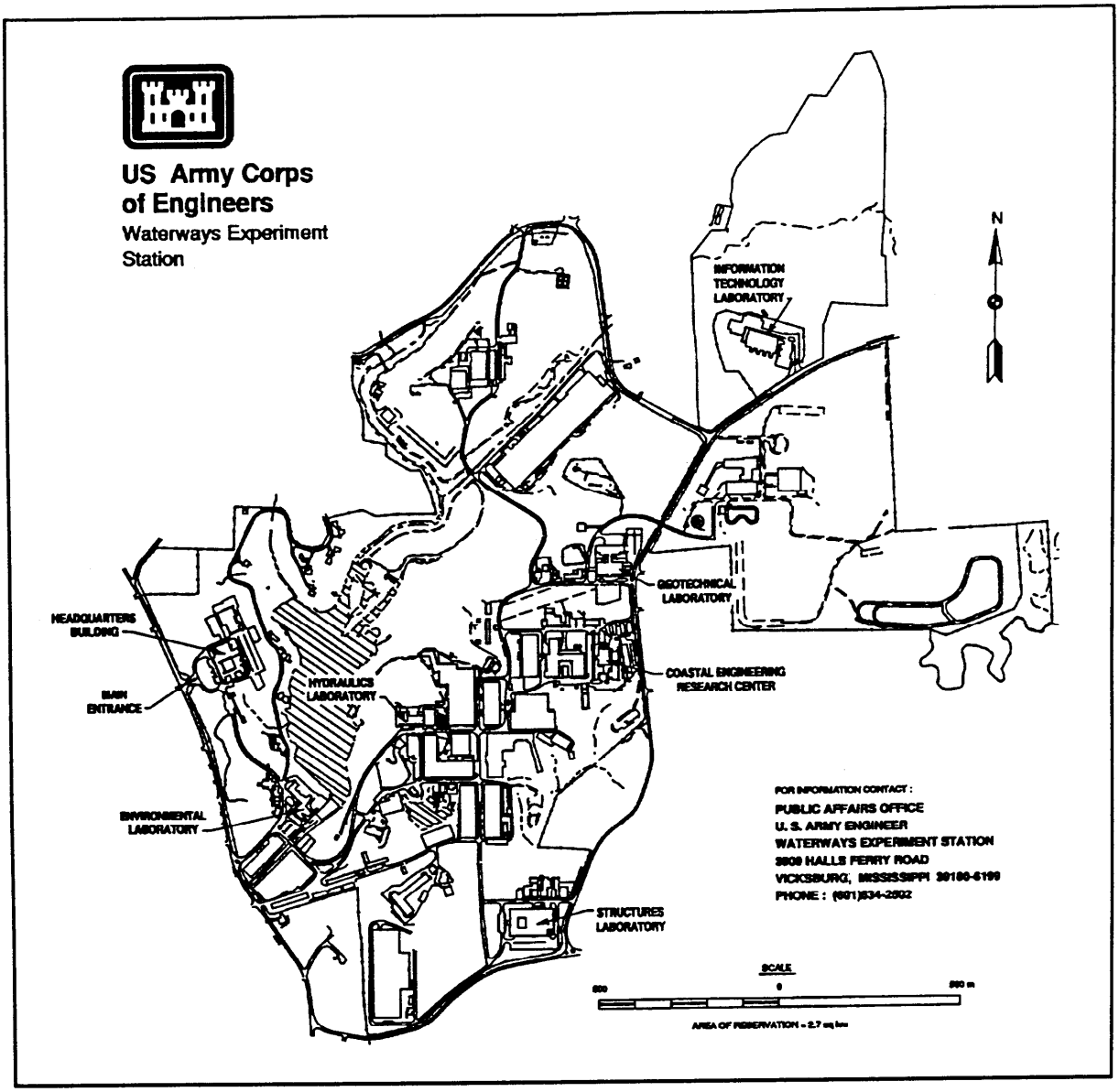

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Contents

Preface

The work reported herein was conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS, as part of the Installation Restoration Research Program (IRRP) and the U.S. Army Environmental Quality Technology Research Program, Work Unit AF25-ET-001.

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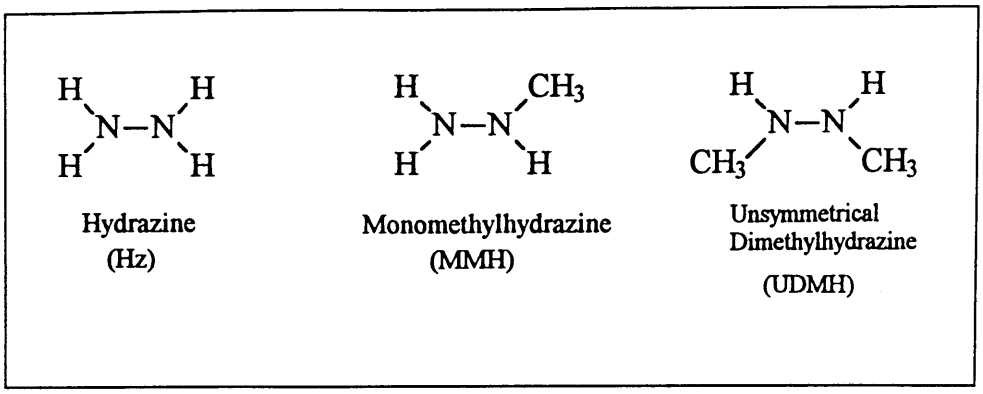
1 Introduction

Hydrazine (Hz) and its methyl derivatives, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), are substances that react with an oxidant without an external ignition source. As a result, these hypergolic compounds are widely used in a number of military and industrial processes. Their use as a rocket fuel was developed by the Germans in World War II. This application has extended to include propulsion systems for modern rockets, spacecraft, and satellites. It is utilized as an oxygen scavenger to reduce corrosion in boilers, metal pipes, and fittings (Patty 1963; Leithe 1971). Other industrial uses for hydrazines are in metal plating (Hepburn 1947) and the manufacture of solder fluxes and pharmaceutical and agricultural chemical production (Schmidt 1984; Schiessl 1980). The development of personal electronic equipment to be utilized by soldiers in the battlefield requires compact and efficient sources of electrical energy. Fuel cells utilizing hydrazine have been proposed as lightweight, portable means of supplying power to electronics (Schmidt 1984). The potential for environmental contamination during manufacture, use, transport, and disposal of hydrazines makes two things necessary: an analytical method for their determination in the environmental at low levels and the determination of the effectiveness of bench-, pilot-, and full-scale remediation schemes for hydrazine cleanup processes.

Hydrazine and the two alkyl derivatives of hydrazine, monomethyl hydrazine and unsymmetrical dimethylhydrazine, are produced and transported in large quantities for industrial and military purposes. The methylated compounds MMH and UDMH are similar to hydrazine in basicity and reaction properties. Mixtures of the three are widely used in rocket fuel formulations.

Hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine are of environmental interest because of their high toxicity. Toxicological routes of entry for these compounds are inhalation, skin absorbance, and ingestion. Symptoms of exposure include irritation and burning of skin, eyes, and respiratory system; liver and kidney damage; and cancer. The National Institute for Occupational Health and Safety considers these hydrazines occupational carcinogens and limits exposure to them at 0.03, 0.04, 0.06 ppm for Hz, MMH, and UDMH, respectively. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended that the threshold limit value (TLV's) be lowered from 100, 200, and 500 ppb, respectively, to 10 ppb each in air (ACGIH 1991). The interest in these low levels of



hydrazine contamination requires a method of detection of hydrazines in the environment at the parts per billion levels.

The chemical similarity of the three hydrazines of interest makes the low level determination of their concentrations in mixtures a challenge. Methods exist that utilize derivitizing agents that form compounds that either absorb ultraviolet radiation or emit light following excitation. The resulting complexes can then be detected by absorbance or florescence detectors (Preece 1992; Collins and Rose-Pehrsson 1994). This approach to the detection of hydrazines in environmental samples is problematic for two reasons. Complex environmental samples often contain amine functionalities that are similar in reactivity to the hydrazines, compete for the derivitizing agents, and produce high background signal. No derivitizing agent exists that forms stable compounds with all three environmentally important hydrazines (Hz, MMH, UDMH). Analysis of all three hydrazines by two separate derivitizations and separations is costly and time-consuming. A gas chromatographic method exists that can measure all three hydrazines in the same analysis (Dee and Webb 1967). This method requires a column packing that utilizes 2-hydrazinopyridine as a component of the stationary phase. These columns are reactive with air, difficult to prepare, and require frequent repacking. They also separate the hydrazine analytes with increasingly unreliable retention times as the column's reactive stationary phase degrades.

Cation chromatography is capable of separating the three hydrazines in their protonated forms based on their interaction with an ionic stationary phase. Using an electrochemical detector, it is possible to detect hydrazine compounds. The direct oxidation of the hydrazine functionality at a gold electrode in a flow through cell results in detection limits that are low compared with those obtained with other methods for detecting hydrazines. The procedure described here allows the separation and quantitation of the concentration of the three hydrazines at low levels in a variety of matrices.

2 Experimental

The methods used to detect the three hydrazines of interest, Hz, MMH, and UDMH, in a variety of environmental samples require matrix specific sample preparation, separation by ion chromatography (IC), and pulsed amperometric detection. The specifics of the method are outlined below, and the analytes determined are listed in Table 1.

Table 1
CAS Numbers and Physical Properties

Analyte	USATHAMA Code	CAS Number	Density	Boiling Point	Retention Time, min
Hydrazine	HZ	302-01-2	1.021 g/ml	114	13.6
Monomethylhydrazine	MMH	60-34-4	0.866 g/ml	87	15.1
Unsymmetrical Dimethylhydrazine	UDMH	57-14-7	0.791 g/ml	63	17.5

Analytical System

Equipment used in sample preparation is as follows: centrifuge and centrifuge tubes capable of spinning 40 g of material at 3,000 RPM, pH 2-12 test strips, syringes and filters, volumetric flasks—various sizes, automatic pipettes, and autosampler vials.

The IC system consists of a Waters Model 510 pump, Waters Model 717 Autosampler, a Hamilton RPX-X200 250 × 4.1 mm Analytical Cation Exchange Column, Waters Post Column Reaction System, and Waters Model 464 Pulsed Electrochemical Detector with a gold-working electrode and a base resistant Ag/AgCl reference electrode. A NEC Powermate 386/25 computer utilizing the Waters Baseline 810 Chromatography Workstation control system controls the IC system and obtains, stores, and processes data.

The eluent is prepared by polishing 940 ml of Milli-Q 18 M-Ohm water through a Baker C18 extraction SPE disk, adding 60 ml acetonitrile (Baker Analyzed HPLC reagent form J. T. Baker), making the solution 0.005 M in

KH_2PO_4 (0.68 g/ℓ), sonication for 30 min in a sonic bath, and vacuum filtration through a 0.22-μM filter. The eluent is degassed by continuous helium sparging before and during use. The 0.1 M NaOH post-column reaction solution is prepared by adding 5.7 ml 50-percent sodium hydroxide to 994.3 ml C18 polished water.

When utilizing electrochemical detection, care must be taken to reduce the background current at all times. Background current can result from a number of sources: reagent purity, system inertness, incompletely degassed mobile phase, matrix effects, electrode condition, and various other factors. The operating parameters for the IC system are described below:

a. Eluent flow rate: 1.0 ml/min.

b. System temperature: 20 to 25 °C.

c. Injection volume: 25 μℓ.

d. Working electrode cleaning potential 500 mV (0.333 sec), pretreatment potential -350 mV (0.333 sec), and measuring potential 100 mV (0.333 sec).

Matrix

This method is applicable in the determination of the three hydrazines in a broad range of matrixes. The method can easily accommodate the measurement of hydrazine concentration in water samples with ranges in purity from distilled water to seawater to heavily contaminated wastewaters. The concentration of hydrazines in organic solvents can be analyzed by this method following an extraction with acidic water. The determination of the amount of extractable hydrazines from soil is possible for this method. Extraction of the hydrazine containing soil with acidic water results in the formation of protonated hydrazines that are highly water soluble. Hydrazine analysis of extracts from sediments, sludges, and slurries is also feasible.

Sample Preparation

In order to analyze the hydrazine concentration in environmental samples, the analytes must be processed to a point where they can be injected into the ion chromatography system. Three general matrix types can be analyzed by this method: waters, solvents, and soils. Samples and extracts are stored in the dark at 4 °C prior to analysis.

Water

Preparing for analysis of samples in water matrix generally involves filtering and, if necessary, dilution with mobile phase followed by injection. A 10-ml polyethylene syringe equipped with a 0.45-μm filter is loaded with approximately 5 ml of the water sample. The sample is filtered and the pH of the filtered sample is measured with a pH strip. If the sample is basic (pH greater than 7), the pH is adjusted with dilute nitric acid (0.1 M) to an acidic pH. This ensures that all hydrazine injected is in the ammonium base form. A test injection of the samples provides a means of determining the rough concentration of the analytes in the sample. If high concentrations of hydrazines are found, dilution of the sample with filtered and degassed mobile phase to a concentration within the calibrated concentration range may be necessary.

Solvents

Organic solvents can be analyzed for hydrazine by extraction with the acidic mobile phase. Addition of acid results in the formation of the hydrazine's ammonium base, which is highly water soluble. By this method, nearly quantitative extraction of hydrazine is possible. Extraction of hydrazines from organic solvents that are miscible with water involves adding 10 ml of mobile phase to 10 ml of sample and shaking to ensure complete mixing. A 10-ml aliquot of methylene chloride is then added. The solution is mixed by shaking and centrifuged. The two layers are then separated. (An additional 10 ml of methylene chloride is added if two distinct phases are not resolved.) At this point, the organic/methylene chloride layer is discarded and the pH of the water layer measured to ensure that the solution is acidic (if not, the procedure is repeated using 10 ml of 0.010 M nitric acid instead of mobile phase). After filtering, a portion of the extract is injected into the IC where the analytes are resolved and detected amperometrically. If the concentration is higher than the high end of the calibration range for the analytes detected, the sample is diluted with filtered and degassed mobile phase.

Extraction of hydrazines from organic solvents that are immiscible with water involves adding 10 ml of mobile phase to 10 ml of sample. To ensure complete mixing, the solution is mixed by shaking, centrifuging, and separating the two layers. At this point the organic layer is discarded and the pH of the water layer measured to ensure that the solution is acidic (if not, the procedure is repeated with 10 ml of 0.010 M nitric acid instead of mobile phase). After filtering, a portion of the extract is injected into the IC where the analytes are resolved and detected amperometrically. If the concentration is above the linear response for the analytes detected, the sample is diluted with filtered and degassed mobile phase.

Soil and Other Soil-Like Samples

Soil samples are prepared by extracting soil with the ion chromatography eluent. Ten grams of soil is placed in a 40-ml centrifuge tube. Thirty milliliters of mobile phase is placed in the sample vial and shaken for 2 min. The extract is clarified by centrifugation and filtration. Following filtration, the pH is measured; if basic, then the extraction is repeated with 30 ml of 0.010 M nitric acid instead of mobile phase. If necessary, the extract is diluted with fresh eluent to decrease the concentrations of the analytes to the calibrated concentration range of the IC. A portion of the extract is then injected into the IC. Samples from other complex matrices are prepared for analysis in a fashion similar to that described for soils.

Concentration Ranges

The tested concentration range is dependent on the matrix in which the hydrazine is being measured. Standards in mobile phase can be tested in the concentration range of 0.025 to 50 μg/ml. Natural waters spiked with standards can be tested in the concentration range of 0.15 to 50 μg/ml. Clean soils spiked with standards can be tested in the concentration range of 0.15 to 50 μg/g. The testable concentration range will vary considerably with the matrix encountered. Generally, the cleaner the sample the less background current is detected at the electrode providing lower detection limits. Samples that are highly contaminated with other contaminants may have much higher backgrounds associated with them and detection limits are considerably higher.

Interferences

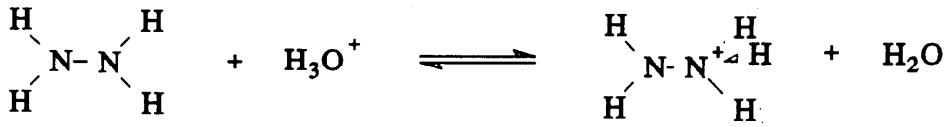
To this point, the only known interference is symmetrical dimethylhydrazine, which coelates with UDMH. Impure reagents, contaminated sample processing, or the presence of other amine-type compounds may result in either interfering peaks or analyte decomposition prior to detection. As mentioned above, analysis of hydrazines from exotic sample matrixes may result in high background current, unidentified interfering peaks, or analyte decomposition prior to detection. Hydrazine measurement by this method may prove to be impossible in these situations and dervitization, extraction, separation, and detection may be necessary. Many of these interferences can be kept to a minimum through the use of rigorously clean reagents and sample processing equipment.

Safety

The analytes are suspected carcinogens, and the partial oxidation products of the alkylhydrazines include nitrosoamines, which are known carcinogens (Baumgarten and Curtis 1982). Good laboratory technique and protective equipment are required during the entire analysis as a result of both the safety risks associated with the analyte and the need to minimize background current arising from contamination. Protective equipment includes impermeable gloves, safety glasses, and fume hoods. Standards and eluents should be disposed of in accordance with approved regulatory practices.

3 Discussion

The basis of the separation in IC is the coulombic interaction competition between the ions being analyzed and the ions in the mobile phase for the charged functional groups on the stationary phase. In this particular system, the mobile phase or eluent contains H_2KPO_4 and HNO_3, so H^+ and K^+ cations are present in the mobile phase at concentrations that are high compared with the hydrazine analytes. The competition for anionic functional groups on the column's stationary phase between these cations and the hydrazine cations formed in the acidic mobile phase (Equation 1) provides a separation mechanism for the three hydrazines.



(1)

Figure 1 shows a chromatogram of the separation of the three hydrazines at 3 ppm. As can be seen, the elution order is hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine. The greater the methylation of the ammonium bases the greater their affinity for the poly(styrene-divinylbenzene) sulfonate ion exchange stationary phase, and, as a result, a separation between the three hydrazines is achieved. Hydrazine is least likely to displace H^+ and K^+ cations and become attached to the stationary phase. The presence of the methyl group in monomethylhydrazine makes this analyte more competitive for anionic stationary phase sites than hydrazine, and, as a result, the monomethylhydrazine elutes later than the unsubstituted hydrazine. The dimethylhydrazines, unsymmetrical dimethylhydrazine, and 1,1-dimethylhydrazine contain two methyl groups and are retained more strongly than the monomethylhydrazine.

As mentioned above, the detection of these hydrazines is problematic because of their chemical composition. No functionalities exist in these molecules that absorb radiation that is typically used for detection in liquid chromatography (visible or ultraviolet). The compounds are not strong conductors, so detection via conductivity does not provide high sensitivity. Their presence in solution can be measured by monitoring the refractive index only at high

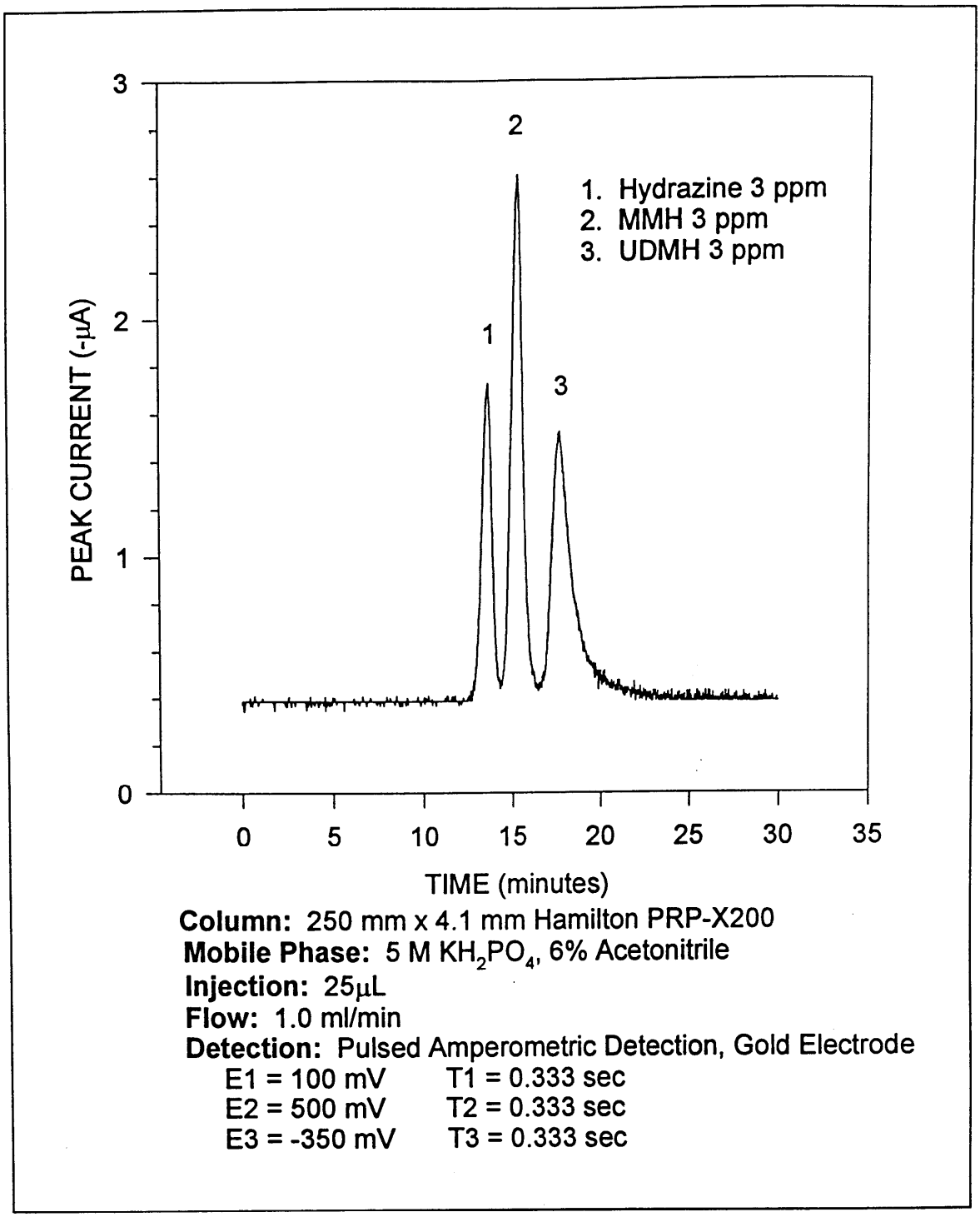
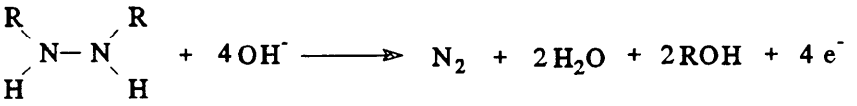


Figure 1. Chromatogram of separation of three hydrazines

concentrations. Compounds containing the hydrazine functionality can be oxidized or reduced at relatively low potentials. This makes their detection by electrochemical methods possible. The electrochemical detector measures the current moving through the electrochemical cell as compounds are reduced or

oxidized at the working electrode. The potential of the working electrode is set at the lowest voltage that oxidizes or reduces the compounds analyzed. The ease of hydrazine oxidation in alkaline solutions at a gold electrode provides enhanced detector selectivity because few compounds are electroactive at a potential of 100 mV. Pulsed amperometric detection provides the ability to operate the working electrode at cleaning, pretreatment, and measuring potentials. By cycling the working electrode through the three potentials, it is possible to provide nearly identical electrode surfaces for each measurement. Thus, electrochemical detection by pulsed amperometry provides a selective and reproducible means of detecting hydrazines following separation by ion chromatography.

The neutral forms of these hydrazines can be oxidized at relatively low potentials on gold electrodes that are electrochemically pretreated at a negative potential. This pretreatment in the basic electrolyte forms a hydroxide-coated electrode surface (Au-OH) on which hydrazine oxidation takes place. Equation 2 contains a proposed oxidation mechanism for hydrazine in alkaline solution (Schmidt 1984):



$$+ \; 4OH^- \longrightarrow N_2 + 2H_2O + 2ROH + 4e^-$$

Hz: $R_1 = H, R_2 = H$

MMH: $R_1 = H, R_2 = CH_3$

UDMH: $R_1 = CH_3, R_2 = CH_3$

(2)

In the above reaction, four electrons are produced for each hydrazine molecule oxidized. The movement of these electrons is measured in the electrochemical cell. The amount of current passed through the cell is proportional to the concentration of the hydrazine anions in solution. This current is then plotted versus time, and the resulting peak heights and areas can be used to determine the amount of the three hydrazines in a given sample.

The concentration range that can be accurately tested by this method is bounded by two extremes because of the nature of the electrochemical detection system. In the first, the concentration of the analyte is so low that it does not produce an oxidation current greater than the noise of the background current. In the second, the concentration is so large that all of the possible electrode sites are occupied, and additional hydrazine molecules pass the electrode undetected.

In a flow-through cell, the actual amount of analyte oxidized depends on the rate of flow through the cell. At a high-flow rate, the working electrode only oxidizes the hydrazine that passes near the electrode surface as the eluent

flows through the detector. At slower flow rates, more of the hydrazine in solution has time to diffuse to the electrode surface to be detected. The ratio of detected to nondetected analyte is proportional to the diffusion coefficient of the analyte in the mobile phase. This diffusion coefficient is not expected to change with the concentration of the analyte in solution. As a result, the current generated at the electrode is directly proportional to the concentration of the analyte in the mobile phase. In the work described here, the flow rate is 1.0 ml/min and, thus, only a portion of the analyte present in the eluent is oxidized at the electrode. Increased sensitivity can be achieved at lower flow rates; however, lower flow rates increase analysis time.

4 Conclusions

A means of separation and quantitation of the three predominant components of hydrazine-based propellants in a variety of environmental matrices has been developed. The system is based on ion chromatography for separation of the three hydrazines: Hz, MMH, and UDMH; post-column derivitization of the cations to their neutral form; and detection by pulsed amperometric methods. The method is capable of detecting hydrazines down to the tens of parts per billion range. This analysis technique is relatively simple, cost efficient, and expected to be a valuable tool for evaluating hydrazine contamination.

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13. ABSTRACT ***(Maximum 200 words)***

A method for the separation and detection of three common industrial and military hydrazines in environmental matrices has been developed. The ammonium bases of hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine are separated by ion chromatography. Detection of the analytes is achieved by pulsed amperometric detection in alkaline solution at a gold working electrode. The method presented provides a fast and cost-effective means of analyzing hydrazines in environmental samples.

14. SUBJECT TERMS

Electrochemistry	Ion chromatography	Pulsed amperometry
Hydrazine	MMH	UDMH
Hz	Monomethylhydrazine	Unsymmetrical dimethylhydrazine
IC	PAD	

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